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X-RAY MICROSCOPY USING SYNCHROTRON RADIATION*

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Present accomplishments in the field of high-energy x-ray microscopy have been reviewed recently.[1] It was pointed out that the x-ray microscope (XRM) is capable of making determinations of trace elements approaching femtogram sensitivity and with lateral resolution of 10 μm or less. Hence, the XRM in its present state of development is becoming an analytical tool which can be used effectively in many ways. On the other hand, there are still many ways in which the XRM can be improved and extended in its areas of applicability. In particular, a combination of approaches which make it feasible to do chemical speciation of trace elements on the μm-scale with the XRM will result in a chemical-speciation x-ray microscope (CSXRM) that will greatly extend analytical capabilities in the chemical sciences.

The system for x-ray microscopy now being developed at the X-26 beam line of the Brookhaven National Synchrotron Light Source (NSLS) is described here. Examples of the use of x-ray microscopy for trace element geochemistry, biology and medicine, and

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materials investigations are given to emphasize the scientific applications of the technique. Future directions for the improvement and further development of the X-26 microscope and of the x-ray microscopy field in general are discussed.

Description of the NSLS X26 XRM

The X26 XRM is representative of the first generation instruments developed at several laboratories. It is based on the use of the continuous x-ray spectrum produced by the 2.5-GeV electron-storage ring of the National Synchrotron Light Source (NSLS). The XRM is used on two different beam lines at locations which are 20 m and 9 m from the x-ray source. Spatial resolution is obtained either by direct collimation of the beam alone or with focussing after the collimator. Beam sizes in either mode of operation have been as small as 5 μm.

The x-ray flux at energies above 5 keV is about 3 x 10^7 photons/(μm^2-s) at a storage ring current of 100 mA at the 20 m location and a factor of five higher at the 9 m station. The flux at the two locations is increased by the use of focussing mirrors that produce an image of the x-ray source at the XRM. Use of the mirrors increases the flux by about 100 - 500, depending on the beam line. The focussed image size at unity magnification is about 250 μm x 750 μm in the horizontal and vertical directions, respectively, at the 2σ width.

The flux per unit energy interval is a maximum at low energies and begins to drop very sharply at energies above 15 keV. Despite the decrease with energy, there is sufficient flux to make measurements on elements as heavy as lead. Naturally, the trace element sensitivity for a given spatial resolution is less at the higher energies.

The most sensitive region for trace element determinations using energy-dispersive detection of the K-shell photons is from about iron to molybdenum. Absolute minimum detection limits of a few femtograms have been achieved.[4]

Scientific Uses of the XRM

The XRM in its present state of development now represents a substantial improvement in several ways over the now-traditional methods of electron microscopy with energy or wavelength dispersive fluorescent x-ray detection and over the ion microprobe. This is not to say that the older methods are obsolete, but that improved approaches are possible for several types of determinations that make it feasible to more completely characterize or investigate substances of interest.

The introduction of the XRM into general scientific applications is resulting because of the close interaction between scientists in different disciplines cooperating on a project of common interest. For best results the developers of the XRM need broad scientific skills which will enable them to pick out scientific areas that can benefit from the XRM and to then play a leadership role in the implementation of specific experiments.

This has been the model used for the work on the BNL XRM. A number of specific examples taken from work in progress at the XRM are displayed here to illustrate this point.

Trace Element Geochemistry Experiments

In trace element geochemistry work measurement of concentrations of the rare earth elements (REE) is difficult when using detection of their L-x rays because of interferences with the K-x rays emitted by lighter elements. The problem is simplified if it is possible

to use K-x rays. The interpretation of the REE concentrations is an important approach to the understanding of the formation and evolution of the Earth's crust. The use of the XRM can, in principle, be of importance in this area of research since the extent of the synchrotron white light spectrum makes it feasible to observe K-x rays from all rare earths.

As an example of performance, a spectrum obtained from the National Institutes of Science and Technology (NIST) Standard Reference Material No. 612 which contains REE at the 50 parts-per-million (ppm) level is shown in Fig. 1. The spatial resolution was 55 μm x 55 μm. The total photon flux incident on the sample was 2 x 10^5 photons/(μm^2-s) above 30 keV energy at a storage ring current of 68 mA. Approximate minimum detection limits of 50 ppm could be obtained under these conditions. This performance is useful for many experiments, for example, Chen, Chao, Minkin, and Back[2] have obtained preliminary results from examination of Chinese ores containing REE from the Bayan Obo deposits. A general examination of the use of synchrotron radiation for REE work has also been reported.[3]

Other recent experiments have utilized the XRM for study of trace element distributions in coal.[4,5] Trace elements in coal are used as markers that can indicate how the coal was formed and to understand the processes by which sedimentary basins are formed. A spectrum obtained from a coal taken in the San Juan basin in New Mexico is shown in Fig. 2. A series of samples taken at different depths in the seam were analyzed and the variation of the trace elements with depth deduced. The results will be interpreted in terms of several models for fluid flow through the sedimentary basin in which the coal lies.

Biomedical Experiments

Mapping of trace element concentrations in bone is well suited to the XRM. The relatively high-Z matrix makes work with the SEM impossible for low concentration measurements. The XRM, however, is easily able to cope with values at the ppm level with good sensitivity. Two specific applications are mentioned here: the study of metals used in cancer therapy and the study of toxic elements, notably lead.

The therapeutic agent, $Ga(NO_3)_3$, is being used to stop bone resorption in hypercalcemia brought on by several types of bone cancer. The mechanisms by which it acts are not known. Determination of the distribution and concentration in bone is necessary to improve the treatment protocols and to find optimum treatment modes. An initial investigation of the distribution of gallium in the rat tibia following administration of $Ga(NO_3)_3$ was carried out at the XRM.[6] This work showed that the gallium concentrated in regions of the bone that were metabolically active and that the concentrations in the bone were dependent on the amounts of gallium administered. Later work is investigating the effects of hormone therapy administered in conjunction with the gallium nitrate. A scan across the diaphysis of a rat tibia from periosteum to endosteum showing the concentration of gallium relative to that of calcium is displayed in Fig. 3. The form of the distribution is affected by the protocol used for the treatment. Systematic investigation of the gallium concentration will give a better understanding of the pharmaco-kinetics of the treatment.

Measurements in bone of the toxic element, lead, are of great importance for improved understanding of the mechanisms by which the lead can affect the nervous and

other body systems. The biological lifetime of lead in bone is of the order of decades so that it can also be an excellent long-term indicator of time-integrated lead exposure. The latter point has stimulated interest in the in-vivo determination of the lead in bone using K- or L-x ray fluorescence methods.

Accurate mapping of the lead distribution in the bone is required not only for the understanding of the basic biological mechanisms, but also for the interpretation of the results of in- vivo measurements. For this reason, a program to measure the lead in thin sections of human tibia has been undertaken. The structure of a thin section of bone near the periosteum is shown in the photomicrograph of Fig. 4. The particular feature of interest in this case is the circular osteon and Haversian canal. The XRM was used to measure the lead levels from the periosteum to the Haversian canal with a spatial resolution of better than 60 μm. The concentration of lead relative to calcium is shown in Fig. 5 for a scan from periosteum through the osteon. It can be seen that the values obtained are strongly dependent on the region of bone measured and that the concentration changes across the osteon. Systematic work to look at different stages of the osteon lifetime and different levels of lead exposure is necessary and is being undertaken.

An example of a possible application of the high-energy x rays is the in-vivo determination of lead in the human tibia. A typical instrument developed at Brookhaven[7] and used for clinical measurements[8] uses a radioactive source, ^{109}Cd, to produce lead K-x rays. The flux at the tibia from a 100-mCi Cd source placed at 4 cm from the bone emitting into an angular range of $\pm$ 10° , corresponding to a solid angle of 0.096 sr, is 6×10^5 photons/(cm^2·s). In contrast, the flux in a 1-keV band of synchrotron radiation at

the 88-keV Cd photon energy is 6 x 10^7 photons/(cm^2·s) even for a bending magent source and about 10^{11} photons/(cm^2·s) for a wiggler source at a ring current of 100 mA. The synchrotron XRM can therefore have useful and novel applications for clinical research employing both the high-energy and low-energy ends of the synchrotron spectrum to produce K- and L-shell vacancies in lead, respectively.

Experiments in the Chemical Sciences

There are many applications for microanalysis in the energy- related chemical sciences. Chemical methods used to treat coal or oil prior to combustion rely on use of catalysts to improve combustion properties and to remove environmentally damaging components such as sulfur. Some initial measurements have begun on these topics employing the multielemental detection capability of the XRM. However, the use of chemical speciation and structure measurements by means of the x-ray absorption near edge spectroscopy (XANES) or extended x-ray absorption fine structure (EXAFS) methods using the XRM will be of equal or greater importance for microchemical work.

Examples of conventional EXAFS spectra are given in Fig. 6 which shows the results obtained on the NSLS X19 EXAFS beam line for MoS_2 and FeS_2 taken by a point-by-point scan through the energy region at the sulfur K-absorption edge. The time for a single scan was around 15 minutes with a beam size that was 4 mm x 15 mm.

It can be seen that major changes will be necessary to the apparatus to make it feasible to operate with spatial resolutions on the order of 10 - 20 μm. One approach that is useful has been put into operation by A. Fontaine et al.[9] at Laboratoire d'Utilisation due Rayonnement Electromagnetique (LURE). They used an optical arrangement which gave

a focussed x-ray beam at the sample, but with an angular dispersion dependent on the energy of the x ray. A position-sensitive detector then made it possible to collect a complete spectrum in a matter of ms. They were successful in studying a time-resolved chemical reaction. The focussed beam makes it possible to study areas of 400 μm diameter.

At the NSLS on X26, use of a 4-crystal silicon monochromator and detection of fluorescent x rays will give resolutions for XANES at a spatial resolution of better than 50 μm and detection limits of 10 ppm.

Future work that makes it possible to do EXAFS and XANES at the μm resolution level on the ms time scale will be of great importance. The sensitivity of the device should be such that it can detect elements at the trace level. This implies that it will be necessary for it to operate with high-efficiency detection of the fluorescent x rays.

Experiments in Materials Sciences

A pilot study is now going on to measure the location of small voids in ceramic materials using the method of computed microtomography (CMT).[10] A very simple apparatus is used.[11] A pencil beam is defined by appropriate collimation and the sample is then translated through the beam for a set of different angular positions. The number of transmitted photons is measured using a CsI(Tl) photon detector operated in current mode.

In the first work that was done the collimator produced a beam that was 15 μm wide in the horizontal dimension and 20 μm tall in the vertical dimension. The first images were of test samples of silicon carbide with a small hole drilled in them at various places in

different samples. It was possible to find voids down to about 10 - 20 μm diameter in samples that were about 2-3 mm thick. An image reconstructed from the scans is shown in Fig. 7. The 250-μm diameter artificial void can be seen at the center of the picture as can several smaller natural voids close to the edges of the scan. This demonstration shows that CMT can be used for nondestructive analysis of ceramics.

Future Directions in X-Ray Microscopy

In the brief examples of experiments in different scientific fields that are given above it can be seen that the XRM in its present form can already be used for many new types of experiments that are not otherwise feasible. It is pleasing to be able to say that there are still many ways in which the XRM can be improved in the future.

Some of the work that needs to be done is quite obvious. It is certainly necessary to optimize the use of all the photons in the beam by using detection systems of maximum efficiency. Improved energy dispersive systems that can handle higher counting rates will be helpful. Wavelength dispersive spectrometers with position-sensitive detectors will help to give better detection limits. Further application of the CMT method and use of coded apertures may help to increase the data taking efficiency and help to relieve the demands on x-ray optics and collimators imposed by the need to improve spatial resolutions.

For the most part these are developments that are aimed at improving the techniques for trace element determinations. A change that seems to be taking place in the field now is the recognition that XRM must not be defined in a narrow sense of trace element detection or even of measurement of density differences as in CMT in the transmission mode. Rather it should be recognized that the XRM will evolve in a way similar to the

SEM or to the use of various techniques for surface analysis that co-exist in a single experimental station. Thus, in a similar way, the XRM of the future will be able to image a material or chemical substance in a variety of independent modes that combine transmission and fluorescence measurements with simultaneous ability to look at the chemical and other parameters of the material through EXAFS, XANES, Auger Electron Spectroscopy (AE), X-ray Photoelectron Spectroscopy (XPS), X-Ray Diffraction (XRD), and electron microscopy is an obvious direction since all of these techniques are now used at synchrotrons, but generally independently on different beam lines. A judicious combination of these methods in a single XRM instrument is a logical next step that should go on in parallel with the other developments of the fluorescence approach.

These thoughts naturally suggest that the addition of other complementary analytical methods could also be considered. The use of low and high energy ion beams for surface analysis and isotopic determinations would be logical. The present size of the ion beam equipment is reasonably small and does not preclude installing them on a typical synchrotron beam line.

New synchrotron radiation sources that are now under construction will have a major impact on the XRM when they start operation about 5-7 years from now. An example of such a new facility is the 7-GeV machine now under construction at Argonne National Laboratory and the similar machine being built at the European Synchrotron Radiation Facility at Grenoble. The use of an undulator-type insertion device will give orders of magnitude improvement in the photon flux that can be delivered to a small area at energies to 20 keV and the wiggler-type insertion devices will do the same at higher energies.

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Figure Captions

Figure 1. Spectrum for NIST Standard Reference Material No. 612 which contains REE at the 50-ppm level. Minimum detection limits are about 50 ppm.

Figure 2. Spectrum obtained from polished section of coal taken from the Lee Ranch Mine in the San Juan Basin region of New Mexico.

Figure 3. Scan across the shaft of thin section of bone from the tibias of two rats showing the change in the Ga concentration relative to that of Ca for two different treatments with $Ga(NO_3)_3$. The endosteum is on the left and the periosteum is on the right.

Figure 4. Photomicrograph of thin section of bone taken from a human tibia. The circular structure is an osteon and associated Haversian Canal. The left edge of the section is the periosteum. The total distance across the specimen is approximately 500 μm.

Figure 5. Scan across the specimen shown in Fig. 4 showing an increase of Pb relative to Ca at the periosteum and at the edges of the osteon for thin sections of rat tibia from vitamin D-deficient rats treated with $Ga(NO_3)_3$.

Figure 6. Typical EXAFS spectrum for MoS_2 and FeS_2 showing the effects of different chemical structures.

Figure 7. Microtomogram of ceramic with void. The pixel size was 10 μm x 10 μm, and the size of the tomogram is 311 x 311 pixels.

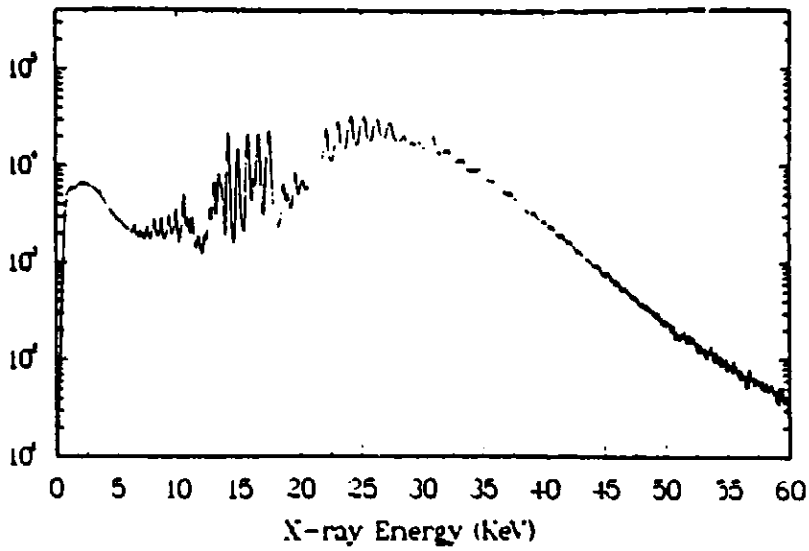

Figure 1

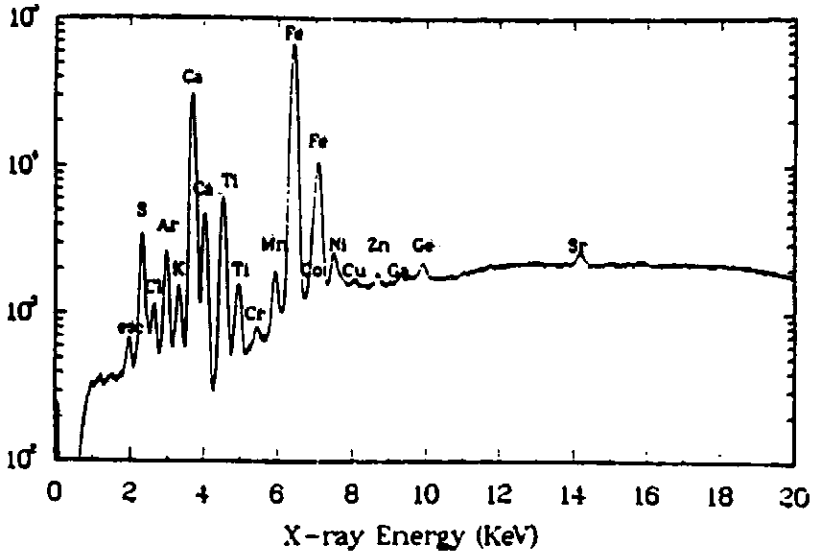

Figure 2

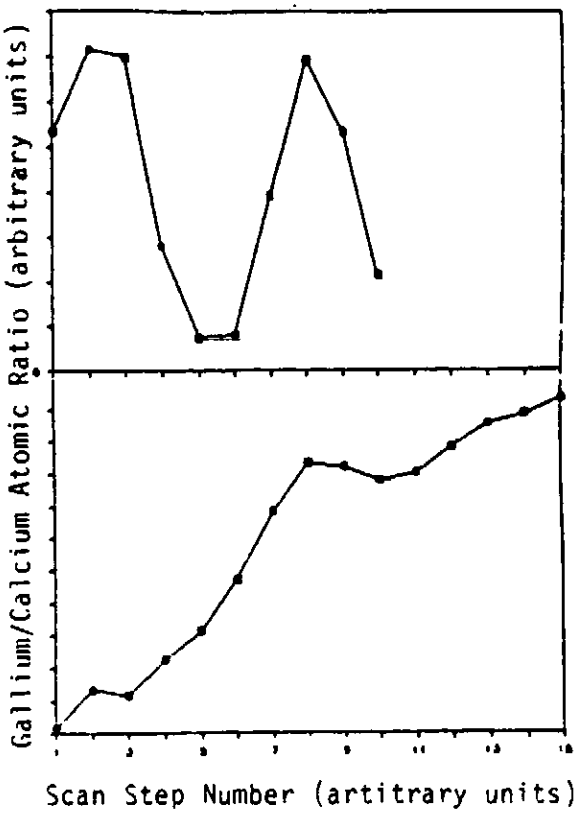

Figure 3

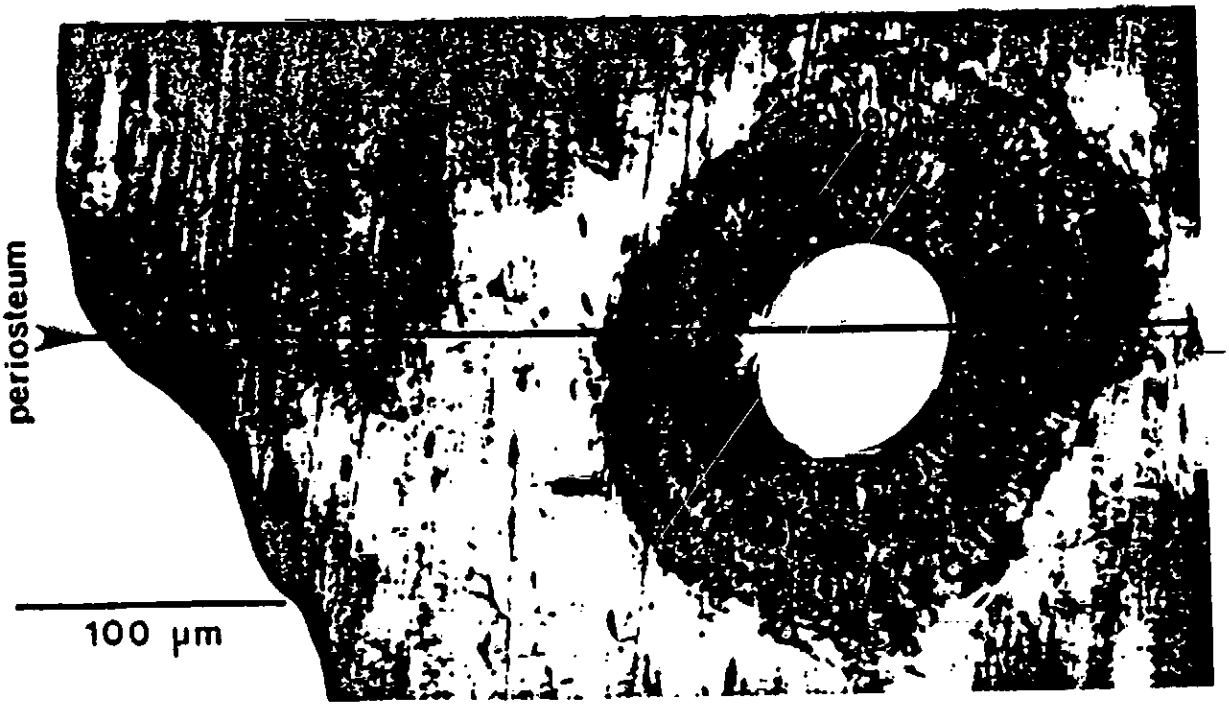

Figure 4

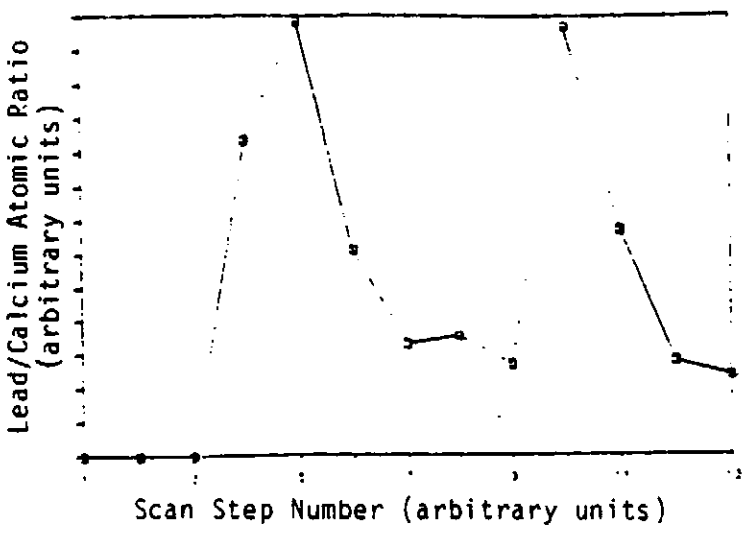

Figure 5

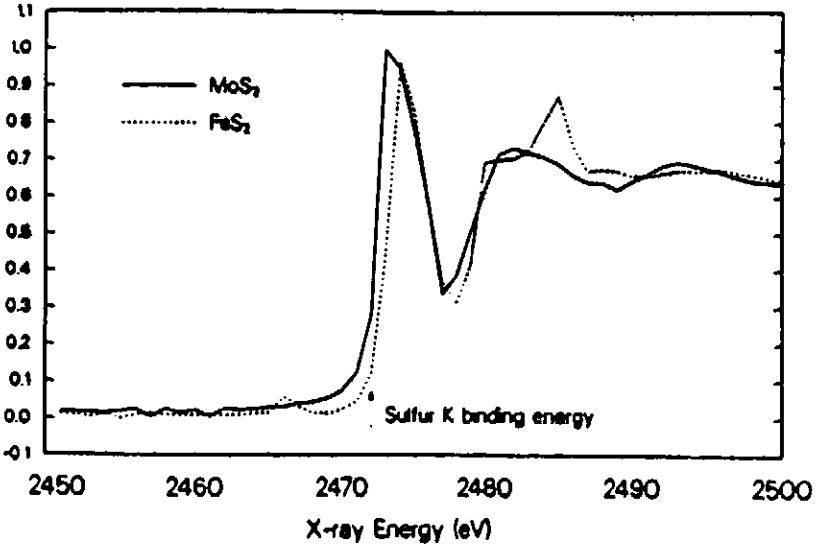

Figure 6

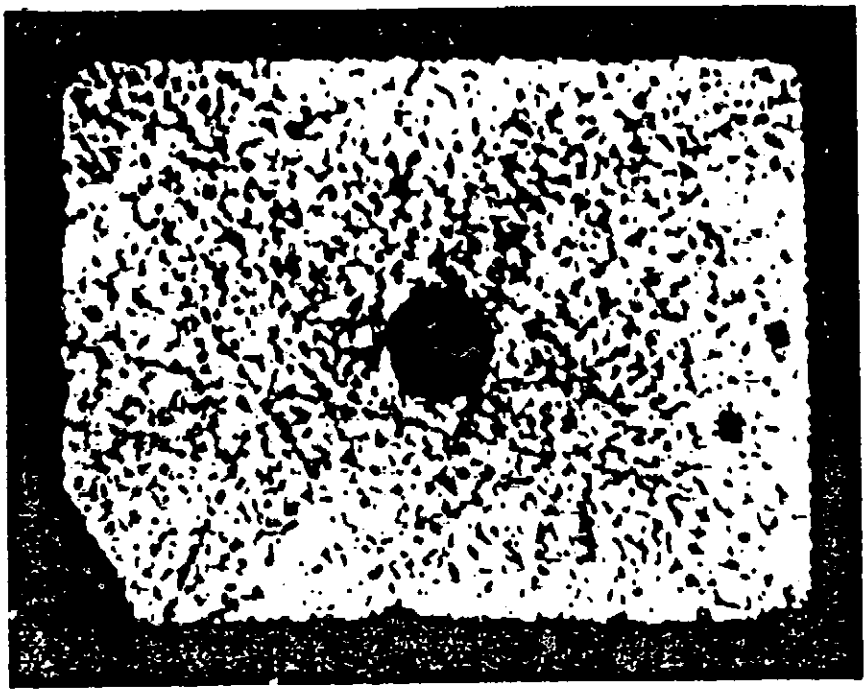

Figure 7